Ninth Edition

Student Solutions Manual to Accompany The Systematic Identification of Organic Compounds

Christine K. F. Hermann • Terence C. Morrill Ralph L. Shriner • Reynold C. Fuson



STUDENT SOLUTIONS MANUAL TO ACCOMPANY THE **SYSTEMATIC IDENTIFICATION** OF ORGANIC COMPOUNDS

STUDENT SOLUTIONS MANUAL TO ACCOMPANY THE **SYSTEMATIC IDENTIFICATION** OF ORGANIC COMPOUNDS

Ninth Edition

CHRISTINE K. F. HERMANN

TERENCE C. MORRILL

RALPH L. SHRINER

REYNOLD C. FUSON



Copyright © 2023 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Trademarks: Wiley and the Wiley logo are trademarks or registered trademarks of John Wiley & Sons, Inc. and/or its affiliates in the United States and other countries and may not be used without written permission. All other trademarks are the property of their respective owners. John Wiley & Sons, Inc. is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data applied for:

Paperback: 9781119799856

Cover design by Wiley

Set in 9/13pt Ubuntu by Straive, Pondicherry, India

Table of Contents

Preface	vii	Problem Set 4	166
Chapter 4 Preliminary Examination,		Problem Set 5	169
Physical Properties, and Elemental Analysis	1	Problem Set 6	172
Chapter 5 Classification of Organic		Problem Set 7	178
Compounds by Solubility	5	Problem Set 8	183
Chapter 6 Separation of Mixtures	13	Problem Set 9	188
Chapter 7 Nuclear Magnetic	23	Problem Set 10	192
Resonance Spectrometry		Problem Set 11	197
Chapter 8 Infrared Spectrometry	45	Problem Set 12	203
Chapter 9 Mass Spectrometry	51	Problem Set 13	207
Chapter 10 Chemical Tests for Functional Groups	55	Problem Set 14	211
Chapter 11 The Preparation		Problem Set 15	218
of Derivatives	73	Problem Set 16	224
Chapter 13 Structural Problems	117	Problem Set 17	228
Problem Set 1	117	Problem Set 18	232
Problem Set 2	120	Problem Set 19	237
Problem Set 3	144	Problem Set 20	242

Preface

For the first six editions of this textbook, no solutions manual was available. As some of the problems presented throughout the textbook are quite difficult, I wrote the solutions manual as an aid to users of the textbook. The textbook contains no problems in Chapters 1, 2, 3, and 12.

I would like to thank Terence Morrill for the answers to Problem Sets 6–20 in Chapter 13, which is available on a companion website. These answers had been in handwritten form for many years. I would like to thank Danielle Davis for her assistance in writing the solutions manual for the seventh edition. I would like to thank Stephen Pond for his patience and support during the preparation of this edition.

Christine K. F. Hermann Radford University

Chapter 4

Preliminary Examination, Physical Properties, and Elemental Analysis

1. Use the values for a nonassociated liquid.

corr bp =
$$167 + \frac{760 - 650 \text{ mm}}{10 \text{ mm}} \left\{ \left(\frac{0.56 - 0.50}{200 - 150} \times (167 - 150) \right) + 0.50 \right\}$$

= 172.72
1,3-dichlorobenzene

2. Use the values for an associated liquid.

corr bp =
$$180 + \frac{760 - 725 \text{ mm}}{10 \text{ mm}} \left\{ \left(\frac{0.46 - 0.42}{200 - 150} \times (180 - 150) \right) + 0.42 \right\}$$

= 181.55
2,3-dichloro-1-propanol $\begin{array}{c} CH_2 - \frac{H}{C} - CH_2 \\ CI & CI & OH \end{array}$

Student Solutions Manual to Accompany The Systematic Identification of Organic Compounds, Ninth Edition. Christine K. F. Hermann, Terence C. Morrill, Ralph L. Shriner, and Reynold C. Fuson. © 2023 John Wiley & Sons, Inc. Published 2023 by John Wiley & Sons, Inc.

- **3.** 285°C
- **4.** 410°C
- 5. Methyl acetate > methyl thioacetate
- 6. 2-Methyl-2-pentanol<3-methyl-2-pentanol<2-hexanol<1-hexanol

7.
$$\operatorname{sp} \operatorname{gr} \frac{20}{4} = \frac{0.989}{0.834} = 1.186$$

 $\operatorname{sp} \operatorname{gr} \frac{20}{4} = \frac{0.989}{0.834} \times 0.99823 = 1.184$
methyl salicylate

- 8. Bromomethane < bromoethane < 1-bromopropane < 1-bromobutane < 1-bromopentane < 1-bromohexane
- 9. 4-Octene>3-octene>2-octene>1-octene
- **10.** Ethyl propyl ether < 1-pentanamine < 1-pentanol < pentanal < methyl butanoate < pentanoic acid

11.
$$n_D^{20} = 1.430 + \left[(35 - 20)(0.00045) \right] = 1.437$$

12.
$$\left[\alpha\right]_{D}^{25^{\circ}} = \frac{26.6}{\left(2.5 \text{ cm}\right) \left(\frac{10 \text{ cm}}{1 \text{ dm}}\right) \left(\frac{0.8 \text{ g}}{50 \text{ mL}}\right)} = 66.5$$
, sucrose

13. Optical purity = $\frac{6.00 - 4.00}{6.00 + 4.00} \times 100 = 20.00\%$

Observed rotation = $+30.00 \times 0.200 = +6.00^{\circ}$

$$\% ee = \frac{+6.00}{+30.00} \times 100 = 20.00\%$$

% of (+) isomer =
$$\frac{4.00}{6.00 + 4.00} \times 100 = 40.00\%$$

% of (-) isomer =
$$\frac{6.00}{6.00 + 4.00} \times 100 = 60.00\%$$

- 14. Methylene chloride with ether, toluene, or hydrocarbons as co-solvents
- 15. Methanol; ethanol

16. mg of C = 10.71 mg of CO₂ ×
$$\frac{12.011 \text{ C}}{44.009 \text{ CO}_2}$$
 = 2.92 mg of C in sample
%C = $\frac{2.92 \text{ mg of C}}{13.66 \text{ mg of sample}}$ × 100 = 21.38% of C
mg of H = 3.28 mg of H₂O × $\frac{2.016 \text{ H}}{18.015 \text{ H}_2\text{O}}$ = 0.367 mg of H in sample
%H = $\frac{0.367 \text{ mg of H}}{13.66 \text{ mg of sample}}$ × 100 = 2.69% of H
%Br = $\frac{3.46 \text{ mg of H}}{4.86 \text{ mg of sample}}$ × 100 = 71.19% of Br
%O = 100 - (21.40 + 2.69 + 71.19) = 4.72% of O
C = $\frac{21.40}{12.011}$ = 1.782 $\frac{1.782}{0.295}$ = 6.04
H = $\frac{2.669}{1.0080}$ = 2.669 $\frac{2.669}{0.295}$ = 9.05
Br = $\frac{71.19}{79.904}$ = 0.891 $\frac{0.891}{0.295}$ = 3.02
O = $\frac{4.72}{15.999}$ = 0.295 $\frac{0.295}{0.295}$ = 1.00
Empirical formula = C₆H₉Br₃O
Empirical weight = 326.86

Empirical rormula = $C_6 H_9 Br_3 O$ Empirical weight = 336.86 Molecular formula = $C_{12} H_{18} Br_6 O_2$

17. a. $C_6H_{12}O_2$

 $U = 6 + 1 - \frac{1}{2}(12) + \frac{1}{2}(0) = 1$ One double bond; *or* one ring

- **b.** $C_5H_{10}Cl_2$ $U = 5 + 1 - \frac{1}{2}(12) + \frac{1}{2}(0) = 0$ No double bonds, triple bonds, *or* rings
- **c.** C₇H₁₃N

 $U = 7 + 1 - \frac{1}{2}(13) + \frac{1}{2}(1) = 2$

Two rings; or two double bonds; or one ring and one double bond; or one triple bond

d. C₁₂H₁₀

 $U = 12 + 1 - \frac{1}{2}(10) + \frac{1}{2}(0) = 8$

Benzene plus three rings; *or* benzene plus three double bonds; *or* benzene plus two rings and one double bond; *or* benzene plus two double bonds and one ring; *or* benzene plus one triple bond and one double bond; *or* benzene plus one triple bond and one ring

Chapter 5

Classification of Organic Compounds by Solubility

- a. N alcohols, aldehydes, ketones, esters with one functional group and more than five but fewer than nine carbons, ethers, epoxides, alkenes, alkynes, some aromatic compounds (especially those with activating groups).
 - **b.** S₁ monofunctional alcohols, aldehydes, ketones, esters, nitriles, and amides with five carbons or fewer.
 - **c.** A₂ weak organic acids; phenols, enols, oximes, imides, sulfonamides, thiophenols, all with more than five carbons; β-diketones; nitro compounds with α-hydrogens.
- **2. a.** Insoluble in water, soluble in 5% sodium hydroxide solution, soluble in 5% sodium bicarbonate solution.

4-methylbenzoic acid



b. Soluble in water and ether, litmus paper turned blue.

butylamine CH₃CH₂CH₂CH₂NH₂

c. Insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution, but soluble in 96% sulfuric acid solution.

3-heptene CH₃CH₂CH=CHCH₂CH₂CH₃

Student Solutions Manual to Accompany The Systematic Identification of Organic Compounds, Ninth Edition. Christine K. F. Hermann, Terence C. Morrill, Ralph L. Shriner, and Reynold C. Fuson. © 2023 John Wiley & Sons, Inc. Published 2023 by John Wiley & Sons, Inc. **d.** Soluble in water and ether; litmus paper is unchanged in color.

CH₃CH₂C^OCH₂CH₃ ethyl propanoate

e. Soluble in water and ether; litmus paper is unchanged in color.

propanenitrile CH₃CH₂C≡N

f. Insoluble in water and 5% sodium bicarbonate solution, but soluble in 5% sodium hvdroxide solution.



- 3. a. A.
 - **b.** S_B **c.** N **d.** S,
 - e. S.
 - f. A.
- 4. Both acyl halides and anhydrides react with water, so any results would be of the carboxylic acid that is formed from the hydrolysis of these compounds.
- 5. a. 1-Propanol is more soluble in water than diethyl ether. 1-Propanol can hydrogen bond with water, whereas diethyl ether does not hydrogen bond with water.

CH,CH,CH,OH CH,CH,OCH,CH, 1-propanol diethyl ether

b. Pentanedioic acid is more soluble in water than butanedioic acid. Odd carbon number of dioic acids have less intracrystalline forces than even carbon number of dioic acids.



c. Methyl methacrylate is more soluble in water than poly(methyl methacrylate). Polymers are insoluble in water.



methyl methacrylate poly(methyl methacrylate)

d. Butanoic acid is more soluble in water than 2-Bromobutanoic acid. The addition of halogens increases the molecular weight and decreases the solubility.



e. 2-Methylpropanoic acid is more soluble in water than butanoic acid. Branching lowers the boiling point and lowers intermolecular forces. Thus, a branched compound is more soluble in water than a straight chain molecule.

$$\begin{array}{cccc} \mathsf{CH}_3 & \mathsf{CH}_2 & \mathsf{CH}_2 \\ \mathsf{CH}_2 & \mathsf{C} & \mathsf{CH}_3 & \mathsf{CH}_2 \\ \mathsf{O} & \mathsf{CH}_3 & \mathsf{C} & \mathsf{OH} \\ \mathsf{O} & \mathsf{OH} & \mathsf{OH} \\ \mathsf{O} & \mathsf{OH} \\ \mathsf{O} & \mathsf{OH} \\ \mathsf{OH$$

a. 1-Chlorobutane is insoluble in water since it is an haloalkane. It is insoluble in 5% sodium hydroxide solution, 5% hydrochloric acid solution, and 96% sulfuric acid solution. Thus 1-chlorobutane is in solubility class I.

1-chlorobutane CH₃CH₂CH₂CH₂Cl

b. 4-Methylaniline is insoluble in water since it is an aniline. It is basic, due to the presence of the amino group, and therefore is insoluble in 5% sodium hydroxide solution, but soluble in 5% hydrochloric acid solution, and thus 4-methylaniline is in solubility class B.

4-methylaniline



c. 1-Nitroethane is insoluble in water since it is a weak organic acid. It is soluble in 5% sodium hydroxide solution, but insoluble in 5% sodium bicarbonate solution, and thus 1-nitroethane is in solubility class A₂.

1-nitroethane CH₃CH₂NO₂

d. Alanine is an amino acid, thus is amphoteric, and soluble in water. Alanine is insoluble in ether and thus in solubility class S₂.

e. Benzophenone is insoluble in water because it has more than five carbon atoms. Since it is a neutral compound, containing only carbon, hydrogen, and oxygen, it is insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution. It is soluble in 96% sulfuric acid solution. Therefore, benzophenone is in solubility class N.

benzophenone



f. As a strong organic acid, benzoic acid is insoluble in water, soluble in 5% sodium hydroxide solution, and soluble in 5% sodium bicarbonate solution. Therefore, benzoic acid is in solubility class A₁.



g. As a saturated hydrocarbon, hexane is insoluble in water, 5% sodium hydroxide solution, 5% hydrochloric acid solution, and 95% sulfuric acid. Hexane is in solubility class I.

hexane CH₃CH₂CH₂CH₂CH₂CH₃

 h. 4-Methylbenzyl alcohol is insoluble in water since it has more than five carbon atoms. It is a neutral compound with only carbon, hydrogen, and oxygen. It is insoluble in water, 5% sodium hydroxide solution and 5% hydrochloric acid solution. However, 4-methylbenzyl alcohol is soluble in 96% sulfuric acid and thus in solubility class N.

4-methylbenzyl alcohol



 As an amine with less than six carbons, ethylmethylamine is soluble in water. It is soluble in ether and its aqueous solutions turn litmus paper blue, therefore it is basic. Ethylmethylamine is in solubility class S_n.

ethylmethylamine CH₃NHCH₂CH₃

j. Propoxybenzene is insoluble in water because it has more than five carbon atoms. It is a neutral compound with only carbon, hydrogen, and oxygen and is insoluble in 5% sodium hydroxide solution, and 5% hydrochloric acid solution. However, propoxybenzene is soluble in 96% sulfuric acid solution and in solubility class N.

propoxybenzene



k. Propanal is soluble in water because it has less than five carbons. As a neutral compound, it is soluble in ether and its aqueous solutions do not change the color of litmus paper. Propanal is in solubility class S₁.

propanal CH₃C

- CH₃CH₂∖_ĆH Ü
- **l.** As an aryl halide, 1,3-Dibromobenzene is insoluble in water, 5% sodium hydroxide solution, 5% hydrochloric acid solution, and 96% sulfuric acid. 1,3-Dibromobenzene is in solubility class I.



m. Propanoic acid is soluble in water because it contains less than five carbon atoms. It is soluble in ether, but its aqueous solutions turn litmus paper red. Propanoic acid is in solubility class S_A.

propanoic acid $CH_3CH_2 \ C \ OH$

As a weak organic acid, benzenesulfonamide is insoluble in water. It is soluble in 5% sodium hydroxide solution but insoluble in 5% sodium bicarbonate solution. Benzenesulfonamide is in solubility class A₂.

benzenesulfonamide

- namide
- o. 1-Butanol is soluble in water because it contains less than five carbon atoms. It is soluble in ether and its aqueous solutions do not change the color of litmus.
 1-Butanol is in solubility class S₁.

1-butanol CH₃CH₂CH₂CH₂OH

p. Methyl propanoate is soluble in water since it contains less than five carbon atoms. It is soluble in ether and its aqueous solutions do not change the color of litmus. Methyl propanoate is in solubility class S₁.

methyl propanoate

CH₃CH₂COCH₃

q. 4-Methylcyclohexanone is insoluble in water since it contains more than five carbon atoms. It is also insoluble in 5% sodium hydroxide solution and 5% hydrochloric acid solution, but soluble in 96% sulfuric acid. Therefore, 4-methylcyclohexanone is in solubility class N.

4-methylcyclohexanone

r. Since 4-Aminobiphenyl is an aniline, it is insoluble in water. It is insoluble in 5% sodium hydroxide solution, but soluble in 5% hydrochloric acid solution.
 4-Aminobiphenyl is in solubility class B.

4-aminobiphenyl

s. Since 4-Methylacetophenone contains more than five carbon atoms, it is insoluble in water. It is also insoluble in 5% sodium hydroxide solution and 5% hydrochloric acid solution, but soluble in 96% sulfuric acid. Therefore, 4-methylacetophenone is in solubility class N.

4-methylacetophenone



t. Naphthalene is insoluble in water since it contains more than five carbon atoms. It is insoluble in 5% sodium hydroxide solution and 5% hydrochloric acid solution. However, naphthalene is soluble in 96% sulfuric acid, and therefore in solubility class N.

naphthalene



u. Phenylalanine is an amino acid, thus is amphoteric, and soluble in water. Phenylalanine is insoluble in ether and thus in solubility class S₃.

phenylalanine



v. Benzoin is insoluble in water since it has more than five carbon atoms. It is insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution. However, benzoin is soluble in 96% sulfuric acid, and therefore in solubility class N.



w. As a strong organic acid, 4-hydroxybenzenesulfonic acid is insoluble in water. However, it is soluble in 5% sodium hydroxide solution and 5% sodium bicarbonate solution. 4-Hydroxybenzenesulfonic acid is in solubility class A,.

4-hydroxybenzenesulfonic acid



7. Listed in order from least basic to most basic (see next question).



- 9. Listed in order from least soluble to most soluble in water.
 - **a.** Smaller alcohols are more soluble.

CH3CH2CH2CH2OH < (CH3)2CHOH <</th>CH3CH2OH <</th>CH3OH1-butanol2-propanolethanolmethanol

b. More hydroxyl groups increase solubility.

CH₃CH₂CH₂CH₃ < CH₃CH₂CH₂CH₂OH < HOCH₂CH₂CH₂CH₂OH butane 1-butanol 1,2-butanediol

c. Branching increases solubility.

 $\begin{array}{c} \mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH} < \mathsf{CH}_3\mathsf{CHCH}_2\mathsf{CH}_3 < \mathsf{CH}_3\mathsf{COH}\\ \mathsf{OH} & \mathsf{CH}_3\\\mathsf{OH}\\ 1\text{-butanol} & 2\text{-butanol} & 2\text{-methyl-2-propanol} \end{array}$

d. $N < S_1 - N < S_B < S_2$

benzaldehyde

3-pentanone

10.	a.	Methanol Isopropyl alcohol Ethanol 1-Butanol	Solubility class Solubility class Solubility class Solubility class	S ₁ S ₁ S ₁ S ₁
	b.	Butane	Solubility class	I
		1,4-Butanediol	Solubility class	S ₂
		1-Butanol	Solubility class	S ₁
	c.	1-Butanol	Solubility class	S,
		2-Methyl-2-propanol	Solubility class	S
		2-Butanol	Solubility class	S ₁
	d.	Ammonium butanoate	Solubility class	S ₂
		3-Pentanone	Solubility class	S₁−N
		Benzaldehyde	Solubility class	N
		Trimethvlamine	Solubility class	S.

11. The following compounds are listed in order of decreasing activity.



Chapter 6

Separation of Mixtures

- 1. a. Pentane volatile
 - **b.** D-glucose low volatility, with certain exceptions these compounds cannot be distilled at atmospheric pressure
 - c. Diethylamine readily distill, many compounds boil below 100°C
 - d. 2-Butanone readily distill, many compounds boil below 100°C
- 2. a. Pentane volatile with steam
 - **b.** D-Glucose not volatile with steam
 - c. Diethylamine volatile with steam
 - d. 2-Butanone volatile with steam

Chlorobenzene, *N*,*N*-dimethylaniline, 2-naphthol, 2-methoxybenzaldehyde



3.

Benzaldehyde, 4-butylaniline, 4-ethylphenol, 4-propylbenzoic acid Organic, 5% HCl Organic Aqueous 4-Butylanilinium Benzaldehyde, 4-ethylphenol, 4-propylbenzoic acid chloride 5% NaOH 5% NaOH Organic 4-Butylaniline Aqueous Benzaldehyde Sodium 4-ethylphenolate, sodium 4-propylbenzoate satd with CO₂ Organic Aqueous 4-Ethylphenol Sodium 4-propylbenzoate 5% HCI 4-Propylbenzoic acid O⁻Na¹ OH OH NaOH satd CO₂ CH₂CH₃ CH₂CH₃ CH₂CH₃ 4-ethylphenol 4-ethylphenol sodium 4-ethylphenolate 0≈_C 0. ₂OH .O[−]Na[†] ∠OH 0. HCI NaOH CH₂CH₂CH₃ CH₂CH₂CH₃ CH₂CH₂CH₃ 4-propylbenzoic acid sodium 4-propylbenzoic acid 4-propylbenzoate NH₃ CI $\rm NH_2$ NH_2 HCI NaOH CH2CH2CH2CH3 CH2CH2CH2CH3 CH2CH2CH2CH3 4-butylaniline 4-butylanilium chloride 4-butylaniline

4.

5. Since glucose is also insoluble in ether, it would be filtered out as Residue 1.

Chapter 6: Separation of Mixtures 15